REACTION OF 1-[2,2-BIS(METHYLTHIO)VINYL]PYRIDINIUM IODIDES WITH ACTIVE METHYLENE COMPOUNDS.

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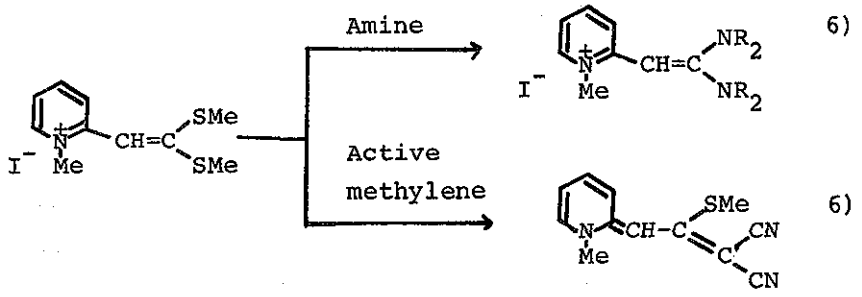
The reaction of 1-[2,2-bis(methylthio)vinyl]-pyridinium iodide derivatives(1b,c) with active methylene compounds in the presence of triethylamine as a base in EtOH gave pyridinium allylide derivatives(2a,b,c) in good yields.

When potassium hydroxide was used instead of triethylamine as a base in dimethyl sulfoxide, the reaction of 1a,b,c with active methylene compounds afforded cleaved compounds of pyridine ring, N-[2,2-bis(methylthio)vinyl]-N-(6,6-disubstituted 1,3,5-hexatrienyl)amine derivatives (3a, b,c,d,e,f,g,h,i) in excellent yields.

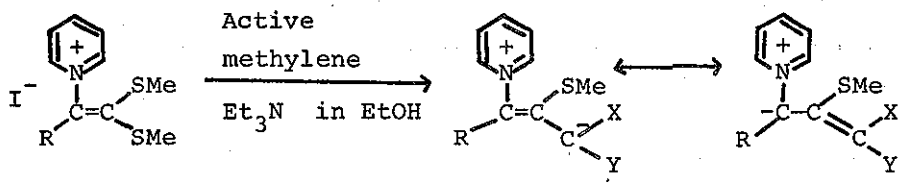
It is well known that ketenethioacetals are attacked by nucleophilic reagents with replacement of either one or two methylthio groups attached to the same carbon atom by such groups as amines or active methylene compounds[1-4].

In our previous papers, we reported that the reaction of heterocyclic ketenthioacetal derivatives, containing a quarternary nitrogen as an electron-attracting group, with nucleophilic reagents (amines and active methylenes) gave the corresponding substituted compounds[5,6].



In our present communication, we report the reaction of 1-[2,2-bis(methylthio)vinyl]pyridinium iodides (1a,b,c) with active methylene compounds in the presence of some bases. These ketenethioacetals (1a,b,c) were prepared by the methods of Krőhnke[7,8].

The reaction of 1b,c with active methylene compounds (malononitrile, methyl cyanoacetate) in the presence of triethylamine as a base in EtOH gave the corresponding substituted products (2a,b,c) of methylthio group in ketenethioacetal derivatives in good yields. However, 1-[2,2-bis(methylthio)vinyl]pyridinium iodide (1a) did not react with active methylenes in a similar condition. Compouds 2a,b,c were well known as pyridinium allylides[9-11] which were useful as synthetic intermediates of indolizine derivatives.



1b,c 2a,b,c

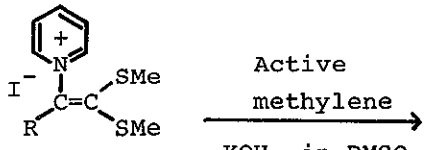
b; R= COPh
c; R= COOEt

2	R	X	Y	mp(°C)	crystal form
a	COPh	CN	CN	192	red plates
b	COPh	CN	COOMe	222	red columns
c	COOEt	CN	CN	172	orange needles

	IR(KBr) cm^{-1}	UV λ_{max}^{EtOH} nm(log ε)
a	2180(CN), 1585(C=O)	262(4.11),324(3.76),4.08(4.28)
b	2180(CN), 1600, 1660(C=O)	262(4.09),332(3.77),4.27(4.16)
c	2170(CN), 1674(C=O)	264(3.69),362(4.16)

When potassium hydroxide was used instead of triethylamine as a base in dimethyl sulfoxide, the reaction of 1c with malononitrile did not give pyridinium allylide 2c but afforded violet needles, mp 164°, in 82% yield. Elemental analysis of this product corresponded to $C_{15}H_{17}O_2N_3S_2$=335.31, and the molecular formula was also suppoted by mass spectrum [m/e: 335(M^+)]. The ultraviolet (UV) spectrum of this compound revealed maximum at 487 nm (10g ε: 4.59) and its infrared (IR) spectrum showed absorption at 3180 cm^{-1} due to amino group, at 2180 and 2190cm^{-1} due to cyano groups, 1715 cm^{-1} due to carbonyl group, and 1620 cm^{-1} due to double bonds. The nuclear magnetic resonance (NMR) spectrum of this compound is shown in Fig. 1.

From these spectral data and elemental analysis, this compound was found to be N-[1-ethoxycarbonyl-2,2-bis(methylthio)vinyl]-N-(6,6-dicyano-1,3,5-hexatrienyl)amine (3f). Similarly, the reaction of 1a,b,c with active methylene (malononitrile, methyl cyanoacetate, cyanoacetamide, and phenylsulfonylacetonitrile) afforded the corresponding ring cleaved products (3a,b,c,d,e,f,g,h,i) in good yield. The ring opening reactions of pyridinium salts are well known[12-16].



1a,b,c

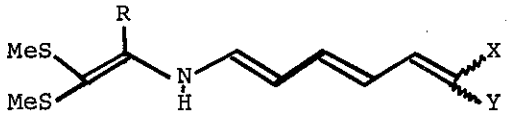
a; R= H

b; R= COPh

c; R= COOEt

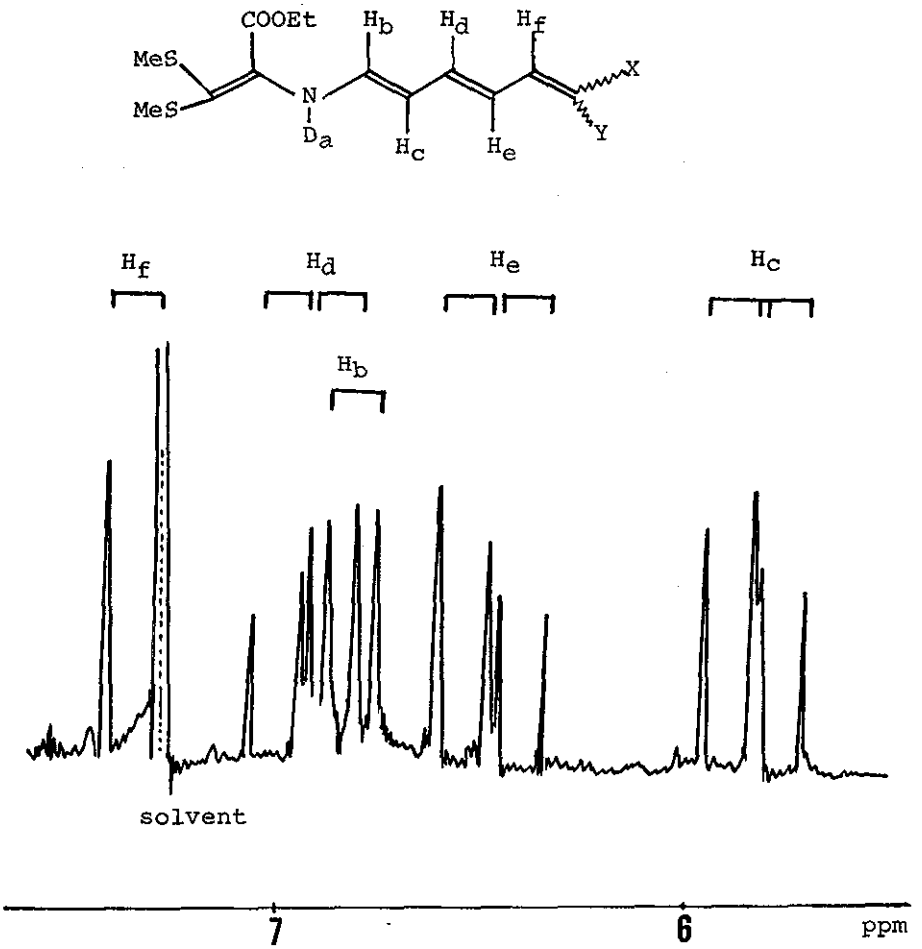
Active methylene

KOH in DMSO



3a - i

3	R	X	Y	mp(°C)	crystal form
a	H	CN	CN	155	violet needles
b	H	CN	COOMe	160	violet needles
c	H	CN	$CONH_2$	172	violet needles
d	H	CN	SO_2ph	165	violet needles
e	COph	CN	CN	233	violet needles
f	COOEt	CN	CN	164	violet needles
g	COOEt	CN	COph	180	violet needles
h	COOEt	CN	SO_2ph	161	red violet needles
i	COOEt	CN	$CONH_2$	165	red needles



N M R spectrum of 3f in $CDCl_3$

(after addition of D_2O)

Fig 1

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